JOURNAL OF THE ROYAL SOCIETY OF WESTERN AUSTRALIA.

VOLUME XXIII.

# 1.—THE ESSENTIAL OILS OF THE WESTERN AUSTRALIAN EUCALYPTS.

## PART IV.

## THE OILS OF *E. OLEOSA*, F. v. M., *E. EREMOPHILA*, MAIDEN, AND *E. LEPTOPODA*, BENTH.

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Read 13th October, 1936; Published 14th May, 1937.

### EUCALYPTUS OLEOSA.

*E. oleosa*, a eucalypt widely distributed in Western Australia, is well known for its polymorphism. As a mallee it is found with rough bark in some districts, and with smooth bark in others. In the goldfields area and southwards it occurs both as a giant mallee and as a tree, each having rough trunk bark. In its tree forms, it grades uniformly into *E. longicornis* and also shows great similarity to *E. Flocktoniae*.

The material used in the present investigation was obtained by Mr. G. H. Burvill from the giant mallee of the goldfields, where it is known as "black mallee." It was collected about the middle of October, 1934, from Fitzgerald Location 55, about six miles north-east of Grass Patch. The bark of the black mallee is dark grey in colour, coarse, rough and persistent; the heartwood is reddish; the leaves are coriaceous, freely dotted with oil glands and the venation is of the typical cineol-pinene type.

Baker and Smith (1920) have described the oil obtained from *E. oleosa* from Nyngan, N.S.W., and a comparison of the results of the two investigations is therefore of interest.

| | Baker and Smith. | Marshall and Watson. |
|---|---|---|
| Yield | 1·1 per cent. | 1·0 per cent. |
| Specific Gravity | 0·923 | 0·936 |
| Refractive Index | 1·4689 | 1·4754 |
| Specific Rotation | — 1·5° | — 7·42° |
| Solubility in 70 per cent. alcohol | In 1¼ volumes | In 1⅛ volumes |
| Saponification value | 4·9 | 7·2 |
| Cineol | 52 per cent. (a) | 45 per cent. (b) |
| Volatility | 78 per cent. volatile below 183° | 65 per cent. volatile below 195° |

(a) by phosphoric acid. (b) by *o*-cresol.

The differences between these oils are similar to those between the specimens of the oil of *E. salmonophloia* discussed in a previous communication (Watson, 1935-36), and are due to the larger proportion of high boiling constituents in the present oil. Both oils contained pinene, aromadendrene, high boiling aldehydes and phenols. In addition, the present oil was shown to contain a considerable amount, probably more than 20 per cent., of geraniol. On distillation, the separation of white solid in quantity, as previously described in this series, was again noted. The fact that Baker and Smith make no mention of this phenomenon, although they observed it

in the cases of two oils of unknown botanical origin, suggests some fundamental difference between the oils of the Eastern and Western Australian varieties of *E. oleosa*.

The oil does not appear likely to be of any medicinal or mining value.

## EUCALYPTUS EREMOPHILA.

*E. eremophila* also occurs in both tree and mallee form, and is distributed through the forest land of the southern interior. The bark is smooth and thin and is silvery grey in colour, with light brown mottling; the heartwood is pale. The leaves are shiny and are copiously and evenly dotted with oil glands; the venation is indistinct, the submarginal vein removed from the edge and indented to meet the roughly pinnate veinlets.

The material used was collected by Mr. G. H. Burvill from small trees on Esperance Location 523, about four miles west-north-west of Scaddan, in the middle of May, 1935; its identity was verified by Mr. C. A. Gardner.

Distillation proceeded rapidly at first and was completed in four to five hours. The oil was pale yellow in colour, had the characteristic odour of cineol-pinene oils, and was obtained in yield of 1.75 per cent. by weight, calculated on thoroughly air-dried material. It contained 33 per cent. of cineol and a high proportion (probably more than 15 per cent.) of *d*-pinene; free acids and esters were present in very small amounts, but alcohols were present in appreciable quantity. Aromadendrene, high boiling aldehydes and small amounts of phenols were also present. The solubility of the oil in alcohol was very low, showing the presence of large amounts of terpenes.

On distillation the separation of white insoluble matter was again noted as boiling commenced; 34.4 per cent. of the oil was volatile below 165°, indicating a high proportion of pinene; 78.2 per cent. was volatile below 195°.

On standing, both the original oil and the various fractions undergo profound physical and chemical changes. There were marked increases in density, refractive index and viscosity which were accompanied by increases in the amounts of free acid, aldehyde and ester present, and by an apparent decrease in the amount of alcohols. Sufficient information is not yet available to give a satisfactory account of these changes.

## EUCALYPTUS LEPTOPODA.

*E. leptopoda* is a mallee which occurs over a wide area in Western Australia; it is found as far west as Cunderdin, Dowerin and Payne's Find; northwards towards Mt. Magnet; eastwards, a little south of the goldfields railway, to Widgiemooltha and Coolgardie, and thence towards the north and east into the mulga country. It is characteristically rather small, generally five to ten feet high, although occasionally as high as twenty feet, and it inhabits poor sand plain soils in association with wodgils.

The material used was collected by Mr. Burvill from Ninghan Location 1341, about eight miles south of Cleary, in the middle of July, 1936, and its identity was established by Mr. Gardner. The leaves were dull, practically linear in shape, 3 to 3½ inches long and about ¼ inch wide, and they were freely dotted with oil glands; the venation was obscure.

The oil, which distilled rapidly, was obtained in 1.3 per cent. yield and was pale yellow in colour. It contained 68 per cent. of cineol, the odour of which was somewhat obscured by the large amount of volatile aldehyde which was present. Pinene, free acids and esters were present in very small amounts, whilst alcohols, calculated as geraniol, made up nearly 11 per cent. of the oil; aromadendrene was present only in small quantity. Both high

and low boiling aldehydes were detected, and, in addition, a phenolic substance, which gave purple coloration with ferric chloride, was present in the higher fractions. The oil contained no phellandrene.

On distillation, insoluble matter again separated as the oil commenced to boil. Little more than 3 per cent. distilled below 162°, but from 162° to 190°, nearly 87 per cent. distilled. The latter material was practically colourless, contained only a trace of aldehyde, had a pleasant odour, and contained 74 per cent. of cineol; its physical properties fall within the required limits of the British Pharmacopoeia and it would therefore make a satisfactory medicinal oil. The scattered distribution of the tree and its sparse foliage, however, would make commercial exploitation perhaps unprofitable.

## EXPERIMENTAL.

### EUCALYPTUS OLEOSA.

Distillation of the oil was fairly rapid and was complete in from three to four hours. The product was pale greenish-yellow in colour and had, in addition to those already given, the following properties:—Acid value, 1.4; ester value: hot, 5.8, cold, 4.1 (corresponding respectively to 2.0 and 1.4 per cent. of esters calculated as $C_{12}H_{20}O_2$); saponification values of acetylated oil: hot, 85.6, cold, 78.4 (corresponding respectively to 22.2 and 20.7 per cent. of alcohols calculated as $C_{10}H_{18}O$).

Redistillation of the oil gave the following fractions:—

| Fraction. | Boiling Range. | Amount. | Specific Gravity. | Refractive Index. | Specific Rotation. |
|---|---|---|---|---|---|
| 1. | Up to 150° C. | 1·5 per cent. | ... | 1·4645 | ... |
| 2. | 150—170° | 16·8 „ „ | 0·8880 | 1·4645 | +19·2° |
| 3. | 170—180° | 33·4 „ „ | 0·9245 | 1·4638 | + 2·0° |
| 4. | 180—195° | 13·3 „ „ | 0·9370 | 1·4714 | — 14·4° |

The residue (35 per cent.) was further fractionated at a pressure of 22mms.

| | | | | | |
|---|---|---|---|---|---|
| 5. | 94—114° | 3·8 per cent. | 0·9639 | 1·4910 | — 44·5° |
| 6. | 114—125° | 6·7 „ „ | 0·9690 | 1·4976 | — 44·4° |
| 7. | 125—160° | 5·3 „ „ | 0·9653 | 1·4991 | — 16·0° |
| 8. | 160—172° | 6·4 „ „ | 0·9807 | 1·5040 | — 2·2° |

From the residue, 5.15 per cent. of white solid was obtained by adding ether and filtering.

Fraction 1 was colourless and strongly acidic. Fraction 2 contained about 45 per cent. of cineol and, when mixed with fraction 1, yielded an appreciable amount (5 to 6 per cent. of the original oil) of *d*-pinene.

Fractions 3 and 4 were practically colourless and contained the greater part of the cineol.

Fraction 5 was colourless and strongly laevorotatory. Its ester value was 32, corresponding to 11.2 per cent. of esters calculated as $C_{12}H_{20}O_2$, whilst the saponification value of the acetylated oil corresponded to 38.2 per cent. of alcohols calculated as $C_{10}H_{18}O$. Small amounts of aldehydes and aromadendrene were also present.

Fraction 6 was also strongly laevorotatory and contained 4.5 per cent. of esters calculated as $C_{12}H_{20}O_2$, and 69.5 per cent. of alcohols calculated as $C_{10}H_{18}O$. It contained larger amounts of aldehydes and aromadendrene than did fraction 5, and gave a strong orange colouration with ferric chloride.

Fraction 7 showed appreciably less laevorotation and contained the maximum amounts of aldehyde and aromadendrene.

Fraction 8 was only slightly laevorotatory; it contained practically no aromadendrene but still contained an appreciable amount of aldehyde; phenols were present in maximum amount.

### EUCALYPTUS EREMOPHILA.

The oil had, in addition to those already given, the following properties:—Specific gravity, 0.9040; refractive index, 1.4724; specific rotation, +11.1°; soluble in 7 volumes of 80 per cent. alcohol; acid value, 0.5; ester value, 0.8; saponification value of acetylated oil: hot, 56.6, cold, 39.7, the latter corresponding to 10.7 per cent. of alcohols calculated as geraniol. The difference between the hot and cold values corresponds to 6.7 per cent. of alcohols calculated as eudesmol. The aldehyde content was 0.058 milligram mol per gram of oil.

On redistillation of the oil, the following fractions were obtained:—

| Fraction. | Boiling Range. | Amount. | Specific Gravity. | Refractive Index. | Specific Rotation. |
|---|---|---|---|---|---|
| 1 | Up to 160° C. | 5·3 per cent. | 0·8779 | 1·4645 | +30·84° |
| 2 | 160—165° | 29·1 „ „ | 0·8778 | 1·4653 | +28·6° |
| 3 | 165—170° | 15·9 „ „ | 0·8889 | 1·4659 | +21·68° |
| 4 | 170—180° | 18·1 „ „ | 0·9014 | 1·4659 | + 8·85° |
| 5 | 180—195° | 9·4 „ „ | 0·9014 | 1·4698 | — 6·16° |

The residue (22.2 per cent.) was distilled under a reduced pressure of 30mms.

| | | | | | |
|---|---|---|---|---|---|
| 6 | 90—125° | 4·9 per cent. | 0·9510 | 1·4860 | —29·2° |
| 7 | 125—150° | 4·3 „ „ | 0·9452 | 1·4984 | — 9·81° |
| 8 | 150—175° | 6·8 „ „ | 0·9579 | 1·5036 | Inactive |

From the residue 1.56 per cent. of white insoluble matter was separated.

Fractions 1 and 2, being very similar to one another, were mixed and redistilled; nearly 13 per cent. (calculated on the original oil) distilled between 156° and 158°, and this had physical properties very similar to those of *d*-pinene. It gave pinene nitrosochloride in quantity.

Fraction 3 was colourless, had a pleasant smell, and contained 35.5 per cent. of cineol.

Fractions 4 and 5 were also colourless and contained respectively 52.5 and 28 per cent. of cineol; their ester values were 11.4 and 12.5 respectively, corresponding to 3.9 and 4.4 per cent. of esters calculated as $C_{12}H_{20}O_2$. The saponification value of the acetylated oil of fraction 5 was 88.2, corresponding to 20.8 per cent. of alcohols calculated as $C_{10}H_{18}O$.

Fraction 6 was very pale yellow in colour, gave positive tests for aromadendrene, and contained an appreciable amount of high boiling aldehyde. Its ester value was 15.4 and the saponification value of the acetylated oil was 231 for both hot and cold hydrolysis; the latter corresponds to 59 per cent. of alcohols calculated as geraniol.

Fraction 7 contained aromadendrene and aldehyde and gave a faint purple colour with ferric chloride. Its ester value was 13.3; on acetylation it gave a product which had hot and cold saponification values of 151 and 122 respectively. The latter corresponds to 29.9 per cent. of alcohols calculated as geraniol, whilst the difference between the hot and cold values corresponds to 11.5 per cent. of eudesmol.

The last fraction still contained some aldehyde together with maximum amounts of aromadendrene and the phenol giving the purple colour with ferric chloride. Its ester value was 11.0; hot acetyl value 116 and cold acetyl value 56. The last figure corresponds to 12.4 per cent. of geraniol and the difference between the hot and cold acetyl values is equivalent to 23.7 per cent. of eudesmol.

### EUCALYPTUS LEPTOPODA.

Distillation of the oil was completed in three hours and the dried product had the following properties:—Specific gravity, 0.9200; refractive index, 1.4662; specific rotation, —0.94°; soluble in 1.8 volumes of 70 per cent. alcohol; acid value, 0.8; ester value, 2.3 (corresponding to 0.8 per cent.

of esters calculated as $C_{12}H_{20}O_2$); saponification value of acetylated oil: hot, 41.6, cold, 38.4. The similarity of the last two figures shows that geraniol is the main alcohol present and the hot value corresponds to 10.8 per cent. of alcohols calculated as geraniol.

The aldehyde content, of which much was low boiling, was equivalent to 0.07 milligram mol per gram of oil.

Redistillation of the oil gave the following fractions:—

| Fraction. | Boiling Range. | Amount. | Specific Gravity. | Refractive Index. | Specific Rotation. |
|---|---|---|---|---|---|
| 1 | Up to 162° C. | 3·3 per cent. | 0·9002 | 1·4575 | + 9·44° |
| 2 | 162—170° | 26·6 „ „ | 0·9060 | 1·4630 | + 8·17° |
| 3 | 170—178° | 51·3 „ „ | 0·9175 | 1·4638 | — 0·30° |

The residue (18.8 per cent.) was distilled under a pressure of 28 mms.

| | | | | | |
|---|---|---|---|---|---|
| 4 | 78— 95° C. | 9·4 per cent. | 0·9266 | 1·4682 | — 7·02° |
| 5 | 95—115° | 5·0 „ „ | 0·9640 | 1·4912 | —28·0° |

From the residue, 2.1 per cent. of white insoluble matter was separated by means of ether.

Fraction 1 was pale yellow in colour, had a strongly irritant odour, was acidic and contained much aldehyde. Only a very small amount of pinene nitrosochloride was isolable.

Fraction 2 contained a trace of aldehyde. The cineol contents of this and the two succeeding fractions were 66, 78 and 73 per cent. respectively, the last two fractions being completely free from aldehyde. Fraction 2 also contained a small amount of low-boiling ester, having a hot ester value of 4.3 and a cold value of nil; in fraction 3 the hot ester value had dropped to 1.3, but in fraction 4 it commenced to rise as higher boiling esters distilled, and in fraction 5, it had risen to 11.0.

The combined fractions 2, 3 and 4 contained 74 per cent. of cineol and had specific gravity 0.915, refractive index 1.4640, and specific rotation + 1.5°.

There was little difference between the hot and cold acetyl values for both fractions 4 and 5. In these fractions, the hot acetyl values were respectively 54.6 and 225, corresponding to 13.5 per cent. and 58.7 per cent. of alcohols calculated as $C_{10}H_{18}O$.

Fraction 5 gave a purple colouration with ferric chloride and contained high-boiling aldehyde; aromadendrene was present in small amount. The residue contained appreciable amounts of high-boiling aldehyde and of the phenol giving the purple colour with ferric chloride; aromadendrene was present in somewhat greater amount than in fraction 5.

The authors are indebted to Mr. G. H. Burvill, of the Department of Agriculture, for the collection of material, and to Mr. C. A. Gardner, Government Botanist, for checking its identity and for the interest he has shown throughout the investigation.

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